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THE PREPARATION OF POLYACETYLENE(U) DEFENCE RESEARCH
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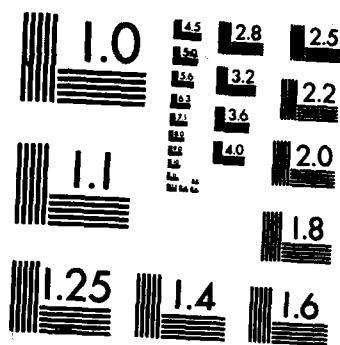
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THE PREPARATION OF POLYACETYLENE

by

A.W. Johnson and A.W. Underdown

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TECHNICAL NOTE 86-7

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November 1985
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Chemical Sources Section
Energy Conversion Division

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ABSTRACT

A procedure for synthesising films of polyacetylene has been described in detail. Photographic evidence for the open fibrillar structure of the material is presented.

RÉSUMÉ

La procédure de synthèse des films de polyacétylène est décrite en détail. L'évidence photographique présentée montre la structure ouverte et fibrilleuse du polymère.



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INTRODUCTION

Polyacetylene $(CH)_x$, is a simple organic polymer with a linear conjugated (unsaturated) structure. It can exist in two forms, cis and trans, which are shown in Fig. 1. $(CH)_x$ is almost entirely cis when synthesised at 77 K, the cis-trans ratio decreasing when the temperature is raised until isomerization to trans- $(CH)_x$ is complete at about 150°C. The polymer can be produced as a thin film or a flocculent precipitate and consists of randomly oriented fibrils about 200 Å in diameter.

Pristine $(CH)_x$ is an insulator, but when chemically doped, its conductivity approaches that of the metals. It has been proposed as a component in Schottky diodes and solar cells and it has potential as the cathode in polymer-electrode batteries. Films of $(CH)_x$ doped with Li^+ , ClO_4^- and $CF_3SO_3^-$ have been used as the anode and cathode in electrochemical cells employing a poly(ethylene oxide)-complex electrolyte and also in non-aqueous liquid electrolyte cells.

Flocculent $(CH)_x$ is produced by bubbling acetylene gas through a catalyst solution, but as films were required for the battery studies associated with this work, a variation of the Shirakawa process was employed. In this method, purified acetylene is admitted into an evacuated reaction vessel containing dissolved catalysts at low temperature. The films formed are removed in a controlled atmosphere box. The details of this method are described in this report.

PROCEDURE

Equipment

A gas handling system, reaction vessel assembly, mechanical pump and cold trap similar to those shown in Fig. 2 and Fig. 3 are required. In addition, an argon-filled glove-box with continuous gas purification, such as Vacuum Atmospheres or equivalent, is needed in which to handle the final product. The atmosphere inside the box must have water vapour and oxygen concentrations of 1 vpm [i.e., no fuming from $TiCl_4$ or $(C_2H_5)_2Zn$; exposed filament burns for 24 h; freshly cut sodium remains bright for 10 min.].

Cleaning the Reaction Vessel

The vessel is washed with hot soapy water and any adherent material remaining from a previous polymerization is removed mechanically. The vessel is then rinsed with distilled water and filled with a concentrated solution of 10% HNO_3 - 90% H_2SO_4 for an overnight soaking. It is then rinsed once with distilled water, three times with acetone from a glass bottle (not plastic) and three times with trichloroethane from a glass bottle.

The side flask is cleaned with dilute HNO_3 , distilled water and acetone. During the cleaning operations, the Rotoflo stopcock is removed.

Materials

The catalyst consists of triethyl aluminum (Aldrich), 25 w/o in toluene, which is used as received, and tetrabutoxy-titanium (Fluka) which is distilled at 140°C and 0.5 Torr. The distillate has a pale yellow or straw colour.

Toluene is distilled under nitrogen and hexane is used as received. Both are stored over 4 Å molecular sieves and sodium chips.

The acetylene is dried as used by passing it through columns of CaCl_2 and P_2O_5 ; a dry-ice trap removes residual acetone which is sometimes present in cylinders of acetylene. The gas is metered by a needle valve in the line and the cylinder is protected by a flash arrester.

The acetylene is purified on the day before it is polymerized.

A spare reaction vessel is attached to the line below the bellow (refer to Fig. 3) and, with valves B,C,D,E and F open, the vacuum line is evacuated for about two hours. E is then closed and the line is considered to be leak-free if there is no noticeable change in mercury levels after one hour.

During the last twenty minutes of this hour, the acetylene line is purged with nitrogen from the cylinder (about one bubble/sec) while valve H is closed.

When the vacuum line is considered to be tight, the nitrogen purge is replaced by acetylene. After 20 minutes of purging, valve H is cracked open slightly so that the system to the left of the manometer slowly fills to one atmosphere pressure (about 5 min). (Valves E and I closed, B,C and D open.) Valve H is then closed and E opened to re-evacuate the line. The discarded acetylene is collected in the cold trap. During this time, acetylene continues to flow through the purification line and vents, through the bubbler, into the fume hood.

t (min)	0	1	2	4	6	7
C_2H_2 (torr)	0	10	27	47	59	67

After 7 min., E is opened to evacuate the reaction vessel. A few minutes later, D is closed and the dry ice is removed.

Following the acetylene purge of the system, acetylene is re-admitted slowly to one atm. as before with E closed and H slightly open. The valve H is then closed and the purification line flushed with nitrogen. At this point, the stopcocks B,C,D and F are open and E,G,H and I are closed.

A dewar of liquid nitrogen is placed around the reaction vessel freezing out the acetylene which is degassed under dynamic vacuum for an hour (E open). Stopcock E is then closed and the dewar is removed to allow the solid acetylene to evaporate. While the vessel is still cold and with the acetylene in a fully gaseous state, B is closed isolating the acetylene for later use. E is opened to evacuate the line, then C and D are closed, the reaction vessel is removed and placed in the glove box.

The line is kept under static vacuum overnight with E closed for leak detection.

Preparation of the Catalyst

The catalyst solution is prepared in the glove box on the day of the polymerization.

Quantities:	Ti(OBu) ₄	1.2 ml
	Et ₃ Al solution	5.5 ml
	Toluene	12.0 ml

The Ti(OBu)₄ and toluene are poured into the reaction vessel and the Et₃Al is added 1 ml at a time over a period of about one minute. The solution turns green at first and then dark brown as the bulk of the Et₃Al is added. The solutions are mixed by swirling the vessel several times. Bubbling occurs and a slight positive pressure is generated. The reaction vessel is transferred out of the glove box and attached to the vacuum line and C is opened to evacuate the dead space above it.

The solution is outgassed by opening D momentarily every few minutes over a period of 30 minutes. A puff of smoke at first appears in the vessel at each opening of the stopcock but ceases after ten minutes. At this point, the solution is briefly swirled between each opening of the stopcock causing bubbles to appear. After 30 minutes a dewar of dry ice and acetene is applied to the reaction vessel and D is opened for ten minutes. No bubbling occurs, even under dynamic vacuum, when the solution is swirled at dry ice temperature.

Polymerization

Following the degassing of the catalyst, stopcocks D and E are closed and B is opened to allow the acetylene into the line from the reservoir.

The polymerization takes place when the acetylene gas comes into contact with the catalyst. To increase the yield of polymer film, the catalyst solution is splashed onto the inner walls of the reaction vessel by shaking it carefully after removing the dewar temporarily. The dewar is replaced and, after waiting to allow the vessel to obtain dry ice temperature, acetylene is admitted by opening valve D.

The typical consumption of acetylene gas with time, in the equipment described, to produce a strong film is as follows:

t (min)	0	1	2	4	6	7
C ₂ H ₂ (torr)	0	10	27	47	59	67

After 7 min., E is opened to evacuate the reaction vessel. A few minutes later, D is closed and the dry ice is removed.

Removal of the Catalyst

Since the purification of the acetylene, nitrogen has been flowing in the purification line. It is now allowed to enter the vacuum line and reaction vessel by closing E and opening H slightly then D. The pressure rises to 1 atm in a few minutes and H is opened fully to permit pressure equalization during the extraction of the catalyst. Excess nitrogen passes through the bubbler to the fume hood.

The catalyst solution is withdrawn through P by means of a long-needle syringe which was previously filled and emptied three times with nitrogen. The used catalyst is discarded.

The punctured septum on P is closed by clamping a new septum, with a greased flat surface on it.

Valve H is then closed and E opened to re-evacuate the reaction vessel.

Washing the Polyacetylene Film

The film is washed with hexane from the side flask. Valve D is closed and I opened momentarily to allow the transfer of hexane vapour and argon into the reaction vessel. Then D is opened briefly to re-evacuate the vessel. This washing procedure is repeated three times.

Finally C and D are closed and I left open; the reaction vessel is removed from the line and placed in a dry ice-acetene bath. The hexane in the side flask is swirled and it distills over. The reaction vessel is removed from the dewar and allowed to come to room temperature while the film soaks in hexane. The hexane is poured back into the side flask and the washing is repeated five times. The film is allowed to soak overnight. If the hexane is still clear the next day, it is transferred to the side flask and I is closed, otherwise, the film is washed again until the solvent is clear.

The reaction vessel is re-attached to the line and evacuated for 2h to eliminate the last traces of hexane. It is then transferred to the glove box where it is opened and any film still adhering to the walls is pried off with a bent glass rod.

The reaction vessel containing the now loose film is taken from the glove box, attached to the vacuum line and re-evacuated. It is removed from the line and the film is washed several times by distilling hexane from the side flask as before.

Finally the film is removed from the reaction vessel in the glove box.

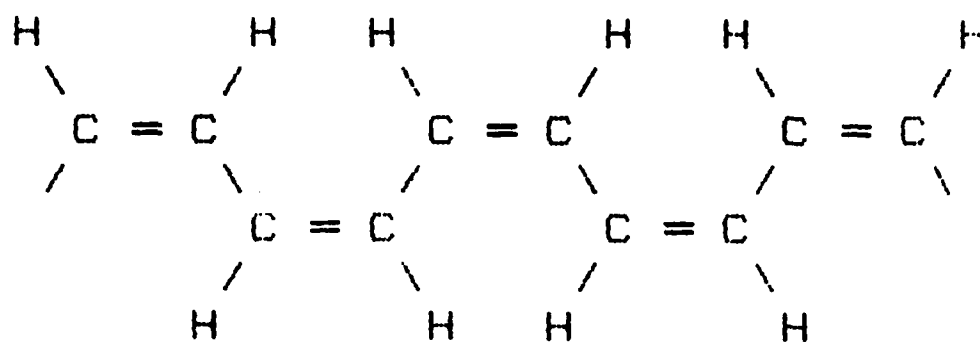
RESULTS

The $(\text{CH})_x$ film which formed on the surface of the catalyst and the wetted walls of the reaction vessel could be removed in one piece. The side of the dark brown $(\text{CH})_x$ which was in contact with the glass walls was shiny with a golden sheen; the opposite side was dull. The thickness varied slightly along the 10 cm length of the cylinder of $(\text{CH})_x$ from 0.02 to 0.06 mm and the average density was 0.21 g/cm^2 . This figure compares well with the published value³ of 0.25 g/cm^3 .

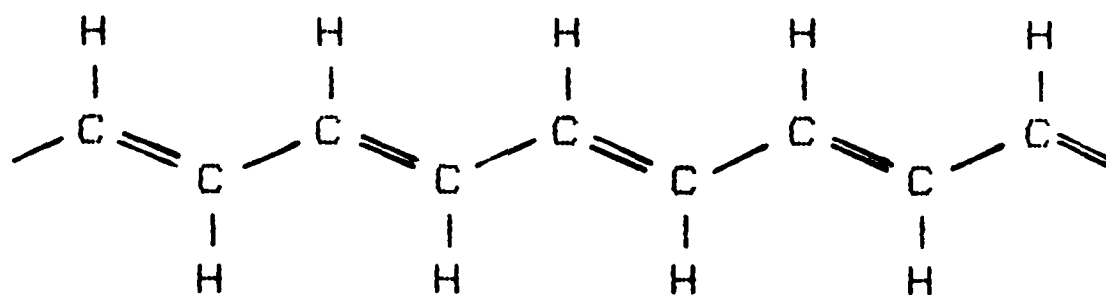
An SEM photograph of the dull side of the film is shown in Fig. 4. It can be seen that the structure is open and distinctly fibrillar with a fibril diameter of $\sim 0.02 \text{ }\mu\text{m}$. The smooth side was firmly packed with little open structure.

REFERENCES

1. S. Etamad et al., Ann. Rev. Phys. Chem. 33, 443 (1982).
2. A.W. Johnson, DREO Report in preparation.
3. M. Maxfield et al., J. Electrochem. Soc. 132, 838 (1985).
4. H. Shirakawa and S. Ikeda, Polymer J. 2, 23 (1971)
5. T. Ito, H. Shirakawa and S. Ikeda, J. Polymer Science 12, 11 (1974).



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FIG. 1 THE STRUCTURE OF cis and trans Polyacetylene

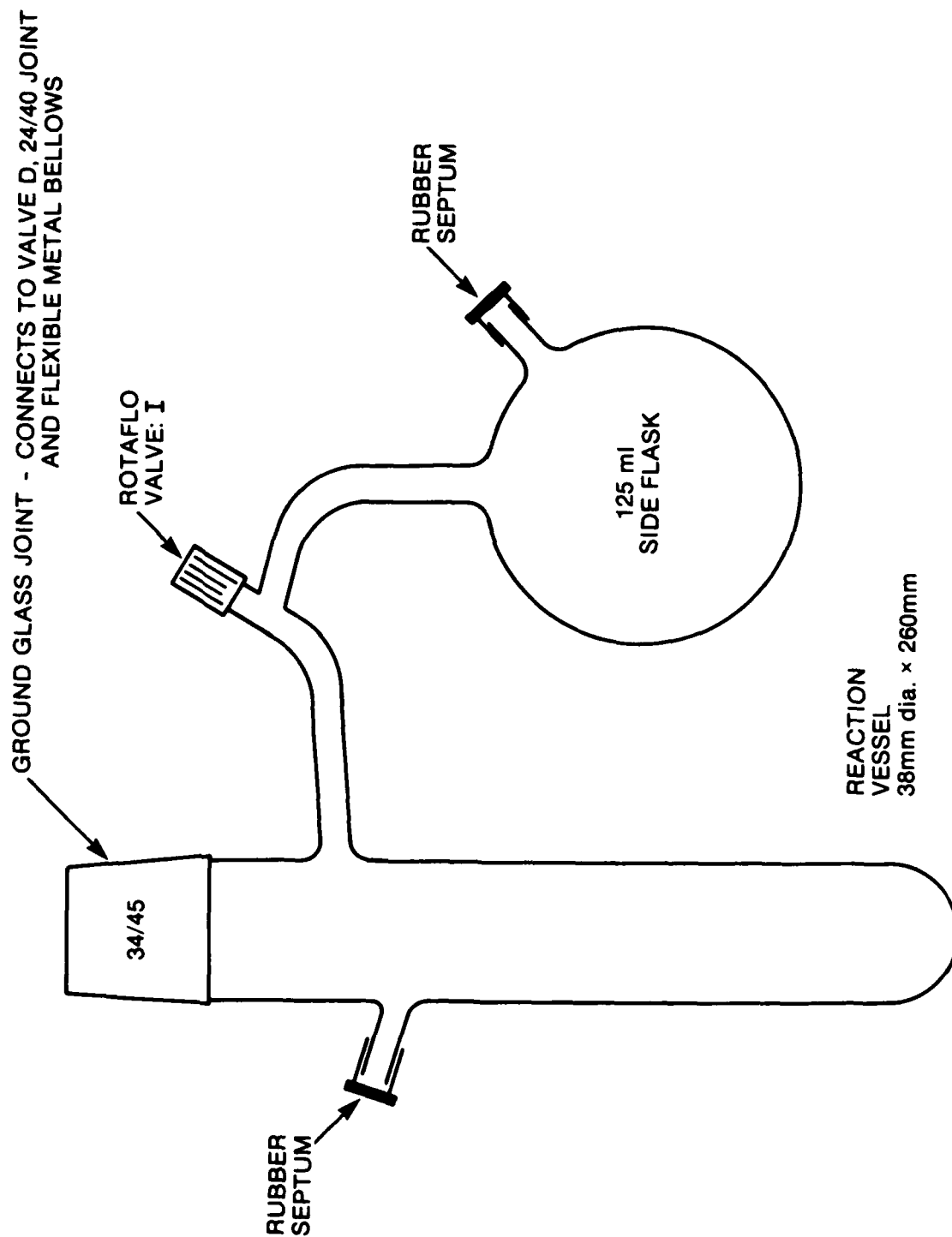


FIG. 2 REACTION VESSEL AND SIDE FLASK

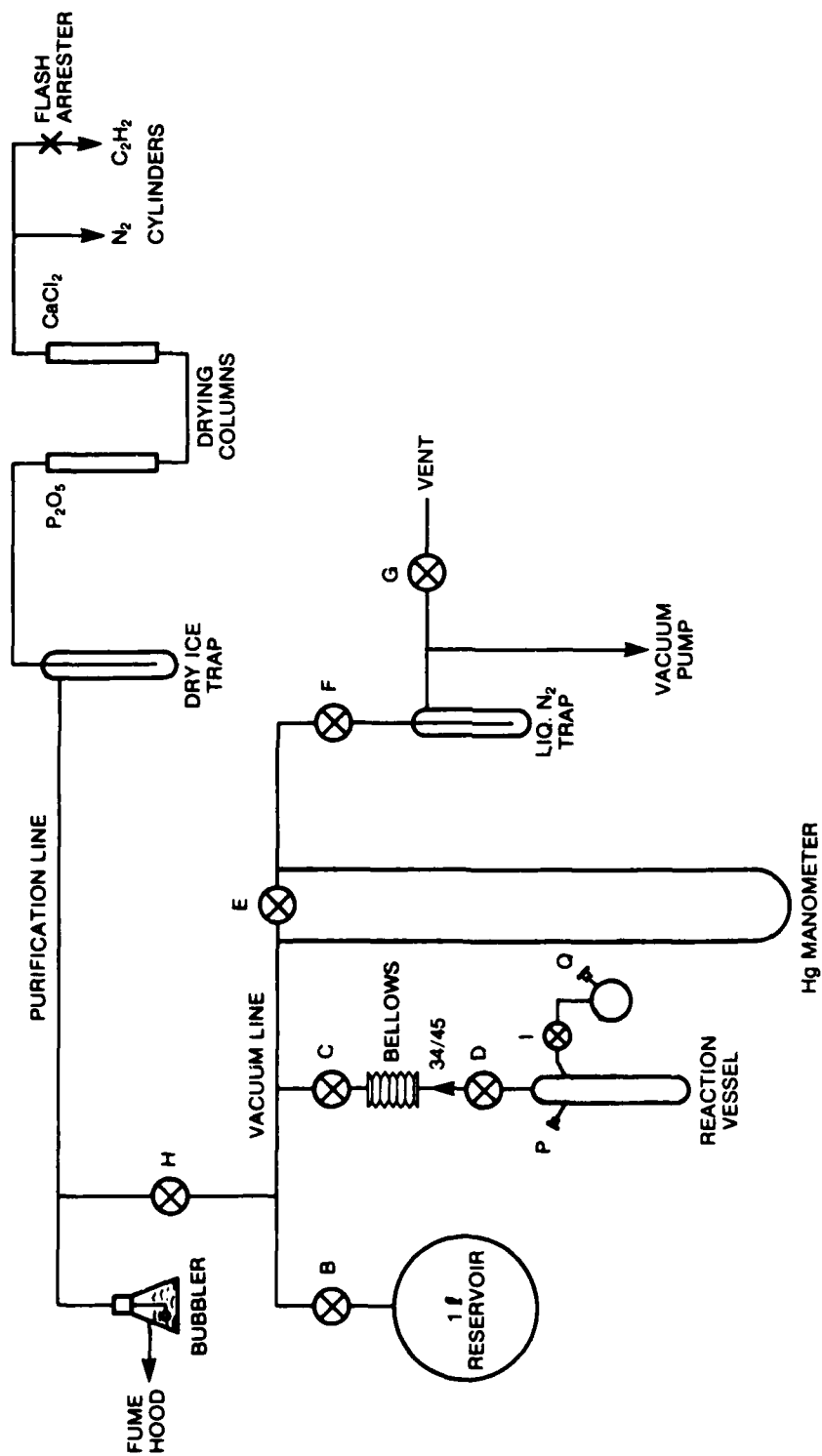


FIG. 3 THE GAS HANDLING SYSTEM



FIG. 4 SEM PHOTOGRAPH OF $(CH)_x$

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13. ABSTRACT A procedure for synthesising films of polyacetylene has been described in detail. Photographic evidence for the open fibrillar structure of the material is presented.		

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